1

## METHOD FOR FORMING POROUS SINTERED BODIES WITH CONTROLLED PORE STRUCTURE

## STATEMENT OF GOVERNMENT INTEREST

This invention was made with Government support under contract no. DE-AC04-94AL85000 awarded by the U.S. Department of Energy to Sandia Corporation. The Government has certain rights in the invention.

## BACKGROUND OF THE INVENTION

The present invention pertains generally to a method for fabricating porous sintered structures and particularly to a method for fabricating sintered foam materials having controlled composition and structure.

Porous structures, metallic as well as ceramic, occupy an important role in technology particularly as materials of construction, heat exchangers, high temperature filters, catalyst supports, and artificial bone and many methods are presently utilized for producing these porous structures. Among the more prominent are conventional powder metallurgical techniques. Generally, powder metallurgical processes involve the steps of shaping metal powder into green compacts by such techniques as loose packing, tamping, compaction, extrusion, rolling or the like and then consolidating the green composite so formed by sintering. Porosity is controlled mainly by particle size, particle size distribution, particle shape and compacting pressure techniques. However, it is difficult to control important physical parameters such as pore size, density and surface area by this technique.

Because of their high strength to weight ratios the class of porous materials known collectively as metallic or ceramic foams are particularly desirable porous structures. However, foams comprising ceramic materials such as magnesia, alumina, silicon carbide, boron nitride and the like; refractory metals such as tungsten or molybdenum; or multiple component materials such as mullite or cermets are difficult to produce. For these reasons, significant effort has been put forth to devise a process to fabricate metallic and ceramic foams.

Metal foam structures can be prepared by blowing a gas through a molten metal followed by rapid solidification to lock in the porous structure or by adding a foaming agent to 45 the molten metal as described, for example, in U.S. Pat. No. 4,713,277. However, it is very difficult to control the porosity in either of these two methods.

As disclosed in U.S. Pat. No. 5,154,970, a open porosity substrate such as a reticulated organic material can serve as a skeleton to define the geometry of the structure. A coating can then deposited thereon, for example, by chemical vapor deposition or dipping as disclosed in U.S. Pat. No. 4,371, 484. The substrate can then be burned or leached out, if desired, thereby forming a foam structure.

U.S. Pat. Nos. 3,946,039, 4,664,858 and 5,248,462 disclose investment casting type processes, and variations thereon, for preparing reticulated SiC or other refractory structures. However, none of these methods can provide microporous foams and, in particular, they cannot be used to 60 produce multiple component foams. Infiltration methods can be used for reducing porosity or pore volume but the process is very time consuming and expensive and it is difficult to achieve uniformity. All these methods of preparing foams or porous materials suffer from the disadvantage that fabrication is difficult and/or time consuming and processing costs are high.

2

Another approach to preparing metallic and/or ceramic foams comprises dispersing metallic or ceramic powders in an organic polymer, thermally decomposing the organic polymer matrix, and sintering the residual powders together.

5 U.S. Pat. No. 4,973,435 discloses dispersing ceramic powder particles in a solution of an organic polymer such as polyacrylonitrile or its coploymers; evaporating the solvent; thermally decomposing the polymer matrix, leaving behind a carbon residue; and sintering the carbon/ceramic powder mixture. The carbon residue from the thermal decomposition of the polymer reacts with the ceramic powder during the sintering step to provide porosity.

U.S. Pat. No. 3,897,221 discloses a method for preparing porous metal structures wherein metal powder is mixed with a solution of polyurethane forming reactants, the polyurethane is caused to gel, the solvent is extracted from the gel, the polyurethane skeleton is removed by thermal decomposition and the metal powder sintered. While this method is capable of forming controlled open pore metal structures it is difficult to produce a uniformly dense structure because of settling of the metal powder during the gelation step. Further, the thermal decomposition of polyurethane leaves a carbon residue that can only be removed by special treatment either during or subsequent to the sintering step.

U.S. Pat. No. 3,833,386 teaches a method for preparing porous ceramic structures by using hydrophilic crosslinked polyurethane foams as a carrier. Generally, an isocyanate capped polyoxyethylene polyol is combined with an aqueous slurry of a sinterable material to which a crosslinking agent can be added, and foaming is effected by reaction of the polyol with water. The rigid foam is thermally decomposed during the subsequent sintering step. This method suffers from the disadvantage that it cannot be used for water soluble or water sensitive materials.

U.S. Pat. No. 5,283,019 discloses a method for preparing porous silicon carbide ceramics using filled polysiloxanes. Here a siloxane is dissolved in an appropriate solvent and SiC powder having a particle size of less than about 10  $\mu$ m is added to the solution. The solvent is evaporated and the resulting powder (a heterogeneous mixture of polymer and SiC powder) is pressed into a shape and sintered. Porosity results from voids left by the thermal decomposition of the siloxane polymer matrix. This method is limited to production of porous SiC bodies and suffers from the disadvantages that it is necessary to ensure SiC particles remain suspended during processing of the solution in order to produce a uniform ceramic, thereby limiting the particle size of metal powder that can be used. The process as disclosed, further requires the step of dissolving the siloxane precursor followed by the step of removing the solvent which necessitates processing solvent and the siloxane polymers employed leave a carbon residue which can be undesirable.

U.S. Pat. No. 5,213,612 discloses a process for making porous tungsten or molybdenum bodies, by mixing together a metal powder, wherein the metal powder has a particle size of 10 µm or less, and a foaming agent and the mixture caused to foam. Foaming is accomplished by mixing a suitable foaming agent, preferably isocyanate capped polyoxyethylene polyol with water. The self-supporting foam/metal product is heated in a reducing atmosphere to thermally decompose the foam and sinter the metal powder. A carbon residue is left from the thermal decomposition of the foam.

U.S. Pat. No. 4,371,484 discloses a method for making porous calcium phosphate bodies by dipping a porous organic material having fine channels into a slurry of calcium phosphate, to which a foaming agent has been added,